(12) UK Patent Application (19) GB (11) 2 058 383 A

(21) Application No 8028990
(22) Date of filing 8 Sep 1980
(30) Priority data
(31) 73350
(32) 7 Sep 1979
(33) United States of America (US)
(43) Application published 8 Apr 1981
(51) INT CL[3] G03C 7/02
(52) Domestic classification G2C A8 C8C1A C8CY
(56) Documents cited
GB 1572658
EP 0009989A
GB 1258320
DT 2708615A
DT 2708537A
(58) Field of search G2C
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(54) Sensitive Photothermographic Material

(57) A silver image and a uniform distribution of an azophenol or azonaphthol image dye capable of being bleached in a silver dye-bleach process are produced by exposing and heating overall a sensitive photothermographic material containing a photosensitive silver salt, a silver halide developing agent, a base release agent and a precursor of the image dye containing a blocked auxochromic hydroxyl group. During heat processing, the base release agent both activates the developing agent and deblocks the blocked hydroxyl group to shift the spectral absorption of the dye. If the silver image and image dye are heated in the presence of a silver complexing agent, an acid and, if necessary, a silver dye-bleach catalyst and/or a thermal solvent, a dye image is formed as a result of the bleaching of the silver image and of amounts of the image dye proportional to the amounts of image silver bleached. The silver dye bleach chemicals can be provided in a layer of the photothermographic material or in a layer of an activator sheet heated in contact with that material. These materials may be used in diffusion transfer processes.

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SPECIFICATION

Sensitive Photothermographic Material

This invention relates to a sensitive photothermographic material.

It is well known to provide a silver image in a sensitive photothermographic material, the material being imagewise exposed, to form a latent image, and heated to a moderately elevated temperature to develop this latent image to a visible silver image.

Photothermographic materials have been proposed for producing dye images. Such materials are described in, for example, U.S. Patent 3,761,270. In these materials a base-release agent releases a base at the processing temperature which enables a reaction between dye-forming coupler and the oxidized form of a colour developing agent, such as an aminophenol developing agent.

Heat-processable photographic materials which produce an image by a silver dye-bleach process have also been proposed, being described in, for example, *Research Disclosure*, April 1976, Item No. 14433, pages 32—34 and *Research Disclosure*, December 1976, Item No. 15227, pages 14—15. These materials contain a sensitive coating which on exposure to light and heating produces a silver image and a bleachable image dye. This dye can be bleached imagewise by heating the material in face to face contact with an activator sheet containing a silver complexing agent, a diffusible acid and, if necessary, a dye-bleach catalyst.

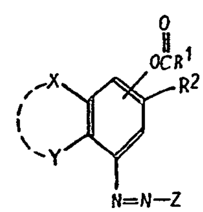
According to the present invention there is provided a sensitive photothermographic material which comprises a support coated on one side with at least one binder-containing layer and, incorporated in the said layer or layers, a photosensitive silver salt, a silver halide developing agent (or a precursor thereof), a base-release agent, and a precursor of an azophenol or azonaphthol image dye capable of being imagewise bleached in a silver dye-bleach process, the precursor containing a blocked auxochromic hydroxyl group which is deblocked by base released by the base-release agent when the material is heated overall to the intended processing temperature.

On imagewise exposure and overall heating to an appropriate temperature, a photothermographic material of the invention gives a silver image and a uniform distribution of the azophenol or azonaphthol dye corresponding to the precursor. This dye can be bleached together with the image silver to form a dye image by a thermal silver dye bleach process. The silver complexing agent, acid and, possibly, catalyst needed for this process can conveniently be provided by incorporating them either in a layer of the photothermographic material or in a layer which is carried by a separate support and held in contact with the photothermographic material.

The deblocking of the blocked auxochromic hydroxyl group of the image dye precursor shifts the spectral absorption substantially, for instance by at least 50 nanometres. The image dye precursor may thus be termed a 'shifted dye'.

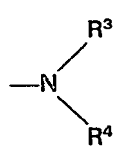
Many azonaphthol and azophenol image dye precursors that contain a blocked auxochromic hydroxyl group, as described, may be used in a photothermographic material according to the invention. Typical azonaphthol and azophenol dye precursors are represented by the structure:

(I)



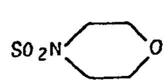
wherein

R^1 is alkyl containing 1 to 20, preferably 1 to 4, carbon atoms, aryl containing 6 to 20 carbon atoms, or



wherein R^3 and R^4 are individually alkyl containing 1 to 10, preferably 1 to 4, carbon atoms or aryl containing 6 to 20 carbon atoms, such as phenyl and naphthyl;

R^2 is hydrogen, SO_2NHR^5 or

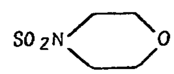


R^5 is hydrogen, alkyl containing 1 to 20, preferably 1 to 6, carbon atoms, or aryl containing 6 to 20 carbon atoms, such as phenyl and naphthyl;

X and Y are individually hydrogen, alkyl containing 1 to 4 carbon atoms, or taken together,

represent the carbon atoms necessary to complete a naphthalene nucleus as represented by the broken line between X and Y;

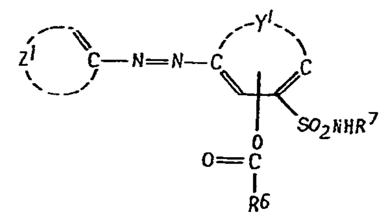
Z is a carbocyclic or heterocyclic group, such as are known in azonaphthol and azophenol dyes; and when R^2 is SO_2NHR^5 or



$$O\overset{\overset{\displaystyle O}{\|}}{C}R^{1}$$

is ortho to the SO_2NHR^5 group.

An especially useful class of dye precursors consists essentially of a shifted azo dye represented by the structure:

(II) 

wherein

Z′ represents the atoms necessary to complete an aromatic, carbocyclic or heterocyclic nucleus containing at least one ring of 5 to 7 atoms;

Y′ represents the atoms necessary to complete a benzene or naphthalene nucleus;

$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-R^{6}$$

is ortho to the SO_2NHR^7 group;

R^6 is a tertiary alkyl group of 4 to 20 carbon atoms or a tertiary amino group of the formula: $-N(R^8)_2$ where each R^8 is independently alkyl of 1 to 10 carbon atoms, such as methyl, ethyl, propyl and pentyl, or aryl or 6 to 20 carbon atoms, such as phenyl and naphthyl; and R^7 is a primary or secondary alkyl group of 1 to 20 carbon atoms, such as methyl, ethyl or decyl, and wherein the dye precursor is capable of being deblocked by means of base released from the described base-release agent upon heating the material containing the dye precursor and the base-release agent to a temperature above 100°C and wherein the resulting dye is capable of being imagewise bleached in a silver dye-bleach process.

Selection of an optimum dye precursor depends upon such factors as the particular processing conditions and base-release agent chosen. A simple test can be useful for selecting the dye precursor. One such test is illustrated in following Examples 1 and 8, the described image dye precursor being replaced with the image dye precursor to be tested.

Illustrative image dye precursors which are useful in photothermographic materials according to the invention are the Compounds 1—11 described in the following Examples.

Useful image dye precursors can be selected from those described in European Patent Applications 0,009,989 and 0,010,001 and in U.S. Patent 3,684,513.

Preferred image dye precursors are those described in European Patent Application 0,010,001 in which the blocking group and a neighbouring group are selected to provide anchimerically assisted hydrolysis.

Certain classes of the described image dye precursors are useful in photothermographic materials in which the resulting image dye upon processing is transferred to an image receiver. Such dyes in a photothermographic material designed for diffusion transfer can contain a monitoring group which in the presence of the base released from the base-release agent and as a function of silver halide development is responsible for a change in mobility of the dye as well as other desired properties. The image dye precursors from which the image dyes are produced can be initially mobile and rendered immobile as a function of silver halide development (such as dye developers), or the image dye precursor can be initially immobile, and rendered mobile in the presence of the base released as a function of heating and as a function of silver halide development. In such compounds the monitoring group can be a ballasted carrier moiety which is cleaved from the dye in the presence of the base release as a function of silver halide development.

In the above structural formulae I and II the aromatic, carbocyclic or heterocyclic nucleus represented by Z and Z′ can be any of the nuclei which are useful in azo dyes. These include phenyl, naphthyl, pyridyl, pyrazolyl, indolyl and pyrazolotriazolyl nuclei. Preferably Z and Z′ represent the atoms necessary to complete a phenyl nucleus which can be substituted with one or more substituents which

do not adversely affect the desired sensitometric properties of the photothermographic material, such as halogen, including chloro, bromo, fluoro and iodo, lower alkyl, lower alkoxy such as methoxy, ethoxy, propoxy or butoxy, or acid or acid derivative substituents such as acids, esters and amides, including, for instance, sulpho, sulphonamido, sulphamyl, carboxy, carboximido or carbamoyl groups which can be unsubstituted or substituted with lower alkyl or phenyl groups. The terms 'lower alkyl' and 'lower alkoxy' are used herein to refer to such groups containing 1 to 4 carbon atoms.

The benzene or naphthalene nucleus comprising X and Y (Formula I) or Y' (Formula II) can contain substituents commonly found in nuclei of azo dyes. These include substituents as just described for the phenyl nucleus completed by Z or Z' as well as other substituents such as nitro, cyano and perfluoroalkyl groups.

The moiety represented by

$$-\mathrm{O}\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{C}}}R^1$$

and

$$-\mathrm{O}-\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{C}}}-R^6$$

in the above formulae is the blocked auxochromic hydroxyl group. If a sulphamoyl group is present, the blocked auxochromic group is joined to the ring in a position which is ortho to the sulphamoyl group. The sulphamoyl group can anchimerically assist removal of the blocking group at the desired time of heating. The blocked auxochromic group must be in conjugation with the described azo group, i.e., ortho or para to the azo group. In a preferred case the blocked auxochromic group is para to the azo group.

Preferred dye precursors of the described formulae are those wherein R^1 or R^6 is a tertiary group. Such a group is believed to provide the necessary bulk to protect the auxochrome from external attack during storage and thereby enhance the storage stability of the dye precursor in the photothermographic materials as described.

Tertiary alkyl groups represented by R^1 or R^6 can be tertiary butyl, tertiary pentyl, tertiary amyl, tertiary dodecyl and tertiary octadecyl groups for example. Tertiary amino groups represented by R^1 or R^6 include dimethylamino, diethylamino, ditertiary butylamino, dipentylamino, methylphenylamino and methyl-para-nitrophenylamino groups, for example. Preferably R^6 is a tertiary alkyl group of 4 to 8 carbon atoms.

Examples of useful R^7 groups include methyl, ethyl, propyl, isopropyl, pentyl, iso-octyl, dodecyl, hexadecyl, octadecyl, carboxymethyl, carboxypentyl, ethoxycarbonylmethyl, and methylsulphamylethyl groups. Preferably R^7 is a primary alkyl group of 1 to 4 carbon atoms. The group R^7 is preferably not a tertiary group or a similar group that will reduce the capability of the sulphamoyl group to anchimerically assist in the removal of the blocking group.

Other useful image dye precursors are described in European Patent Application 0,009,989. In this application image dye precursors are described which comprise moieties which are blocked with a grouping which, upon heating in the presence of the base-release agent, are cleaved from the compound in intramolecular nucleophilic displacement.

The image dye precursors as described can be prepared by procedures known in the photographic art. Typical procedures are described in the European Patent Applications 0,009,989 and 0,010,001 see for instance, Examples 1 to 3 of the latter application.

The described image dye precursors may be used in a range of concentrations in a photothermographic material of the invention. Preferably the concentration of dye precursor is within the range of 0.01 to 1.0 mole of image dye precursor per mole of sensitive silver salt in the photothermographic material. An especially useful concentration of dye precursor is within the range of 0.05 to 0.2 mole of image dye precursor per mole of sensitive silver salt.

The described photothermographic materials contain a photosensitive silver salt, preferably photosensitive silver halide, due to its high degree of photosensitivity. Useful photosensitive silver halides include, for example, silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide, and mixtures thereof. Silver iodide is also considered to be a useful photosensitive silver halide. Photosensitive silver halide can be regular grain photosensitive silver halide. Negative type photosensitive silver halide can be especially useful; however, direct positive photosensitive silver halide can also be used. Preferred photothermographic materials according to the invention contain a silver bromide or bromoiodide gelatino emulsion.

The photosensitive silver halide can be prepared *in situ* in the photothermographic material if desired. Such a method of preparing photosensitive silver halide is described in, for example, U.S. Patent 3,457,075.

The photosensitive silver salt, preferably photosensitive silver halide, may be used in a range of concentrations in the described photothermographic materials. Typically the coverage is from 10^{-4} to

10^{-1} mole of a silver halide per square metre of support. The preferred coverage of a photosensitive silver halide is equivalent to 100 to 2000 mg of silver per square metre.

Many silver halide developing agents, or developing agent precursors, may be used in the described photothermographic materials. Useful silver halide developing agents include, for example, polyhydroxybenzenes, such as hydroquinone developing agents, including, for example, hydroquinone, alkyl-substituted hydroquinones, such as tertiary butyl hydroquinone, methyl hydroquinone, 2,5-dimethyl hydroquinone and 2,6-dimethyl hydroquinone; chlorohydroquinone or dichlorohydroquinone; and alkoxy substituted hydroquinones, such as methoxy hydroquinone and ethoxy hydroquinone; catechols and pyrogallol; methyl hydroxynaphthalene; and methyl gallate. If a polyhydroxybenzene developing agent is selected, it is necessary that it be sufficiently active to provide the desired developing action, especially if the dye is to be bleached in a dye bleach reaction in the photothermographic material. In selecting an optimum developing agent, it can often be useful to provide a combination of developing agents, such as a combination of an ascorbic acid developing agent with a polyhydroxybenzene developing agent. Other developing agents which can be useful alone or in combination in the described photothermographic material include aminophenol developing agents, such as para-aminophenol; reductone developing agents, such as anhydrodihydropiperidino hexose reductone and 3-pyrazolidone developing agents. In many cases 3-pyrazolidone developing agents are especially useful. Such 3-pyrazolidone developing agents include, for example, 1-phenyl-3-pyrazolidone, 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and other 3-pyrazolidone developing agents described in, for example, British Patent 930,572. Combinations of such developing agents can be especially useful if desired.

A developing agent precursor is a compound which releases a silver halide developing agent upon an appropriate change in conditions such as an increase in temperature.

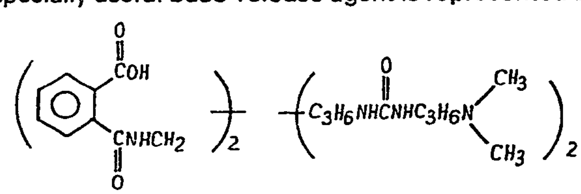
The silver halide developing agent or combination of silver halide developing agents (including any precursor present) may be used in a range of concentrations in the described photothermographic materials. Typically, the concentration of developing agent is within the range 0.25 to 4 moles of silver halide developing agent per mole of the sensitive silver salt material. When a mixture of developing agents is used the total concentration is preferably within this range.

The described dye precursor is deblocked with the aid of a base-release agent. The base-release agent must provide at the processing temperature, normally within the range 100°C to 200°C, a base which is sufficiently active and is present at a sufficient concentration, to enable the desired deblocking reaction to occur and also to enable the developing agent to develop a latent image in the photosensitive silver salt. Many base-release agents may be used to provide the desired reaction conditions at processing temperature in the photothermographic material. Examples of useful base-release agents include guanidinium compounds, quaternary ammonium compounds, such as quaternary ammonium malonates, particular amino acids, such as 6-aminocaproic acid and heat-cleavable hydrazides and oxazolidones which release a suitable base moiety upon heating. Such base-release agents are described in, for example, U.S. Patent 3,531,285. Other useful base-release agents include those which are ionic compounds formed by the reaction of an acid and a base or by ionic exchange using nonionic compounds. Other useful base-release agents, also known as activator precursors or activator stabilizer precursors, include compounds described in, U.S. Patent 4,060,420 such as bis(2-amino-2-thiazolinium)methylenebis(sulphonylacetate) and 1,3-bis[2S-(N,N′-ethyleneisothiourea)ethyl]ureaethylene bis(sulphonylacetic acid), and 2-carboxycarboximides described in U.S. Patent 4,088,496 such as 1,3-bis(2-amino-2-thiazolinyl)propane . N,N′-ethylenebis(phthalamic acid). Aminimide base-release agents can be especially useful.

Some of the described base-release agents and other described addenda may have limited solubility in aqueous formulations and may require some added solvents in preparation of the described photothermographic materials to enable a desired coating composition.

An activating concentration of base-release agent is necessary in the photothermographic material as described to produce deblocking of the described dye precursor and activation of the described developing agent at the processing temperature. A useful concentration of base-release agent is typically within the range of 10^{-2} to 10 moles per mole of sensitive silver salt, from 10^{-1} to 5 moles per mole of silver salt being particularly preferred.

Selection of an optimum base-release agent or base-release agent combination will depend upon the described factors. An especially useful base-release agent is represented by the structure:



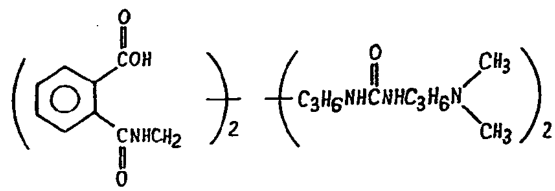
The photothermographic materials as described contain a binder or binder mixture. In some instances a constituent of the photothermographic material can be formed in a solution of the chosen binder during preparation of the coating composition merely by mixing the necessary reactants. For

example, a base-release agent containing an acid and a base moiety can be formed by mixing the acid and the base portions in a binder solution.

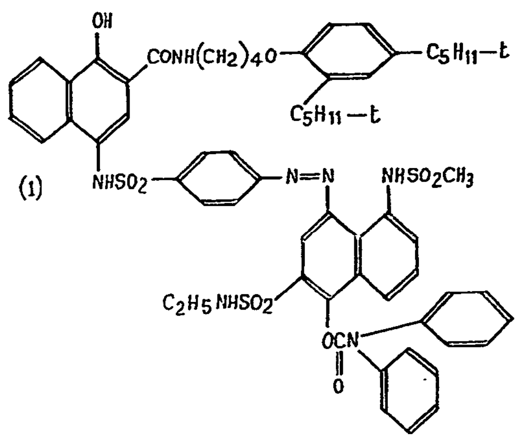
Various binders useful in a photothermographic material of the invention including both naturally-occurring substances and their derivatives, for example, gelatin, and gelatin derivatives, cellulose derivatives and polysaccharides such as dextran and gum arabic; and synthetic polymeric materials, such as water soluble polyvinyl compounds like poly(vinyl pyrrolidone), and acrylamide polymers. The described photothermographic materials can also contain, alone or in combination with the described binders or vehicles, other synthetic polymeric binders or vehicles, such as dispersed vinyl compounds, for instance in latex form, particularly those which increase the dimensional stability of the photothermographic materials.

The photothermographic compositions as described can be coated on a variety of supports. Useful supports are those which can withstand the processing temperatures to be used during development and which do not adversely affect the sensitometric properties of the materials of the invention at those processing temperatures. Typical useful supports include cellulose ester, poly(vinyl acetal), poly(ethylene terephthalate), and polycarbonate films, glass, paper and metal. Preferably a flexible transparent support is used.

An especially useful photothermographic material of the invention comprises a support having thereon, in binder, (a) photosensitive silver halide in reactive association with (b) a 1-phenyl-3-pyrazolidone silver halide developing agent, (c) an activating concentration of the base-release agent represented by the structure:



and (d) the image dye precursor Compound 1 represented by the structure:

(1) 

Another especially useful embodiment of the invention is a photothermographic material designed to produce a dye image by a thermal silver dye-bleach process. This material comprises a support having thereon at least one layer (A) comprising, in binder, (a) photosensitive silver halide, (b) a silver halide developing agent, (c) an activating concentration of a heat-sensitive base-release agent, (d) an azonaphthol or azophenol shifted image dye precursor having a blocked auxochromic hydroxyl group which is deblocked by base released from the base-release agent, and, contiguous to layer (A), at least one silver dye-bleach activator layer (B) comprising, in binder, (e) at least one silver halide complexing agent, (f) a thermal solvent, (g) at least one silver dye-bleach catalyst, and (h) an organic or inorganic acid, wherein said layer (B) has an effective pH less than about 6.0.

Many silver halide complexing agents may be used in the photothermographic material just described for use in a silver dye-bleach process. The complexing agent may be a silver halide solvent, i.e. a compound which, when employed in an aqueous solution at 60°C is capable of dissolving more than ten times the weight of silver halide which can be dissolved in water at 60°C. Typically useful silver halide solvents include water soluble thiosulphates, such as sodium thiosulphate, potassium thiosulphate, ammonium thiosulphate, thiourea, ethylene thiourea, such water-soluble thiocyanates as sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate and water soluble sulphur containing dibasic acids. Diol complexing agents which may be used include, for example, 3,6-dithia-1,8-octanediol; 3,6,9-trithia-1,11-undecanediol; 3,6,9,12-tetrathia-1,14-tetradecanediol; 9-oxo-3,6,9,12,15-tetrathia-1,17-heptadecanediol; and 9,12-dioxa-3,6,15,18-tetrathia-1,20-eicosanediol.

Water-soluble sulphur-containing dibasic acids which may be used as complexing agents include, for instance, ethylene-bis-thioglycolic acid; 3,6,9-trithiahendecanedioic acid; and 3,6,9,12-tetrathiatetradecanedioic acid. The complexing agent selected must be one that does not desensitize the silver halide. In some instances it can be desirable to include a portion of the complexing agent in the layer containing the photosensitive silver halide. Complexing agents which can be incorporated in that layer include, for instance, thiuronium and isothiuronium compounds, such as 2,2′-methylsulphonylaminobis(ethylisothiuronium para-toluenesulphonate); 3,5-thiuronium-1-methyl-1-propane sulphonate; and 3,5-thiuronium-1-propane sulphonate. Certain azo thioethers and blocked azoline thiones may also be used as complexing agents. Combinations of complexing agents may also be used.

The photothermographic material can contain a thermal solvent to aid in processing. The term "thermal solvent" is used herein to mean a non-hydrolyzable organic material which is a solid at ambient temperatures (about 20°C), but which has a mixed melting point with other ingredients at or below the temperature of thermal processing. Especially useful thermal solvents include a variety of ethers, sugars and alcohols which act as solvents for substances incorporated in the photothermographic material. Examples of useful thermal solvents are non-hydrolyzable polar solvents containing up to 10 carbon atoms, such as ethylene glycol and low molecular weight polyethylene glycol, polyethylene oxide, 1,10-decanediol, 1,6-hexanediol and sorbitol. Combinations of thermal solvents can also be useful.

The photothermographic material designed to produce a dye image in a silver dye-bleach process can contain a silver dye-bleach catalyst. Useful catalysts include phenazine, pyrazine, quinoxaline and anthraquinone dye-bleach catalysts which oxidize metallic silver to silver ion. Phenazine is an especially useful silver dye-bleach catalyst in a photothermographic material as described.

The mechanism by which the dye image is produced by a silver dye-bleach process in the photothermographic material is not fully understood. It is believed, however, that upon heating after imagewise exposure of the photothermographic material that a silver image is produced from photosensitive silver salt. The catalyst, after the base-release agent releases base and deblocks the dye precursor, oxidizes the metallic silver to silver ion. The resulting reduced catalyst cross-oxidizes with the dye from the dye precursor and so decolorizes that dye.

The described photothermographic material designed for a silver dye-bleach process contains an acid in the layer containing the complexing agent. A mixture of acids may be used if desired. The acid is preferably a non-volatile acid to avoid release of undesired materials but must be mobile and diffusible in the photothermographic material to permit the silver image to be effectively reached within a reasonable period of time. The acid can be, for instance, a non-volatile diffusible mineral acid or an organic acid containing up to 10 carbon atoms. An acid is useful providing that the processing temperature is lower than that which can vapourize the acid from the photothermographic material but high enough to permit migration of the acid to the layer containing the photosensitive silver halide. Non-volatile mineral acids which are useful include, for instance, sulphuric acids, sulphamic acid and phosphoric acid. Non-volatile diffusible organic acids which are useful include carboxylic acid, such as citric acid and acetic acid, and other kinds of acid including para-toluene sulphonic acid, phenylphosphonic acid, phenyl phosphoric acid, phenyl phosphinic acid, benzene sulphonic acid and para-toluene sulphinic acid, Para-toluene sulphonic acid is especially useful.

The acid in the photothermographic material is preferably strongly acidic and present in a sufficient quantity to provide an effective pH of less than 6.0 and especially less than pH 4.0.

The polymeric vehicle or binder useful in the described layer containing the silver complexing agent is preferably a film-forming polymeric compound containing organic residues which are non-hydrolyzable or slow to hydrolyze. Such useful polymeric materials include poly(vinyl alcohol), poly(acrylic acid), poly(styrene sulphonic acid), poly(vinyl pyrrolidone) and poly(ethylene oxide. It is especially useful to have the vehicle be non-hydrolyzable or slow to hydrolyze because hydrolyzable binders or vehicles, such as gelatin, compete for hydrogen ions and become hydrolyzed and denatured by the presence of the acid in the layer containing the complexing agent. With a vehicle containing hydrolyzable groups, the resulting layer would be less effective for short periods of time after coating on the support.

A "non-hydrolyzable" binder in a photothermographic material of the invention designed for silver dye-bleach process is such that the layer containing that binder and the diffusible acid, when kept at room temperature, i.e., about 19°C and 50% relative humidity, for about 4 weeks, shows no appreciable loss in activity due to pH changes caused by, for example, transesterification or other undesired reactions.

The strength and proportion of the acid in the layer containing the complexing agent can be adjusted to achieve the desired pH range and the use of the thermal solvent can lower the melting point of acids having higher melting points in order to achieve the desired silver dye bleaching.

If gelatin is used as a binder, due to its buffering activities, more acid can be useful in the layer containing the complexing agent. Binders which are not buffers in the silver dye-bleach reaction may require the use of less acid.

The acid may be used in a range of concentrations in the layer containing the silver complexing

agent. Typically, the cover age of acid is within the range of 1.0 g to 50 g per square metre of support. The polymeric vehicle in the layer containing the acid is typically present at a coverage of 1.0 to 50 g per square metre of support. Typical coverages of complexing agent are within the range of 1.0 g to 50 g per square metre of support or within the range of 1 mole to 5 moles of complexing agent per mole of the sensitive silver salt. Thermal solvents can be present at the coverage which is typically within the range of 1.0 g to 50 g per square metre.

A typical layer containing the described complexing agent comprises the following components: (a) thiourea as the complexing agent, (b) 1,6-hexanediol as the thermal solvent, (c) para-toluene sulphonic acid as the acid, and (d) poly(vinyl pyrrolidone) as the binder. Each of the components a—c is typically present at a coverage of 5.4 per square metre of support and the binder is present at a coverage of about 2.7 g per square metre of support. If desired, a surfactant can be added to the described layer to provide better coatability. The composition is typically mixed with a solvent such as a mixture of methanol and water for coating on the desired support. The resulting layer containing the complexing agent has an effective pH of 4.0 or less. In this example the layer contains no silver dye-bleach catalyst due to the low pH of the layer. If desired, a silver dye-bleach catalyst can be added to the layer to provide a more effective result in the silver dye-bleach process upon heating.

A silver image and the adjacent dye in a photothermographic material as described for use with a silver dye-bleach process are bleached by merely heating the photothermographic material. Alternatively, the silver and dye can be bleached by merely placing an activator sheet containing the complexing agent; acid, etc. over the layercontaining the silver image and dye and laminating by applying heat at the melting point of the components and light pressure by means of a roller or otherwise.

The described photothermographic materials can contain a spectral sensitizing dye or combination of dyes to confer additional sensitivity to the photosensitive silver salt.

After suitable imagewise exposure of a dye-bleach photothermographic material of the invention, an image can be developed by heating the material to a temperature within the approximate range of 100 to 200°C, typically a temperature within the range of 125 to 175°C until a desired dye image is provided. In some instances a second heating step can be useful in which the described silver dye-bleach process occurs.

An image is typically developed by heating the photothermographic material to a temperature within the described temperature range for from 1 to 90 seconds, and usually from 1 to 30 seconds. By increasing or decreasing the temperature, a shorter or longer processing time can be achieved.

Various means may be used for heating the photothermographic material after imagewise exposure. The photothermographic material can for instance be brought into contact with a simple hot plate or iron, or with heated rollers, or heated with dielectric heating means.

Small concentrations of moisture can be present during processing such as the concentrations of moisture present in conventional photographic paper supports at atmospheric conditions (e.g. 25°C and 40% relative humidity).

Another embodiment of the invention is a diffusion transfer, photothermographic material wherein the dye produced upon heating can be transferred to a dye receiver. A typical diffusion transfer photothermographic material according to this embodiment comprises a support having thereon, in sequence, (I) a layer comprising, in binder, (a) photosensitive silver salt, especially photosensitive silver halide, in reactive association with (b) a silver halide developing agent, (c) a dye precursor having a blocked auxochromic hydroxyl group as described herein, and (d) an activating concentration of a heat-sensitive base-release agent, and (II) an image receiving layer, preferably an image receiving layer comprising a mordant for a dye image from layer (I).

Instead of incorporating the receiving layer as a layer II in a diffusion transfer photothermographic material according to the invention, the receiving layer can be part of a separate receiver element, such as an image receiver layer coated on a suitable support.

Mordants are preferably present in image receiving layers used for the invention. Useful mordants can typically comprise polymeric ammonium salts, such as those described in U.S. Patent 3,709,690.

In a diffusion transfer process according to the invention, the dye produced upon heating the layer containing the described dye precursor can be transferred, such as in a separate heating step, to the image receiver. This transfer can be carried out typically at a temperature within the range of 100°C to 150°C.

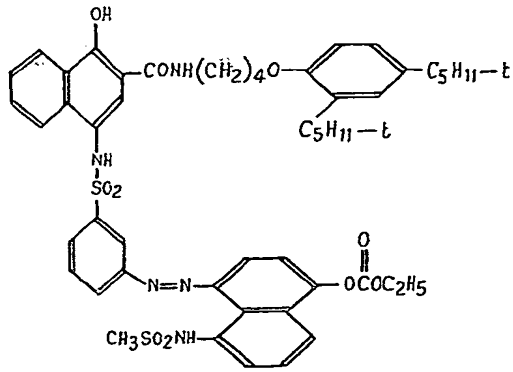
The following examples are included for a further understanding of the invention.

Example 1

Thermal Deblocking of Shifted Dye Precursor

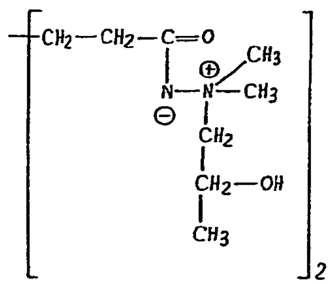
A light insensitive coating was prepared by mixing the following components and coating them on a poly(ethyleneterephthalate) film support at the designated concentrations:

(1) shifted dye Compound 2 represented by the structure:



g/m^2
2.15

(2) heat releasable nucleophile (base-release agent) represented by the structure:



g/m^2
2.15

(3) gelatin (binder) 4.3

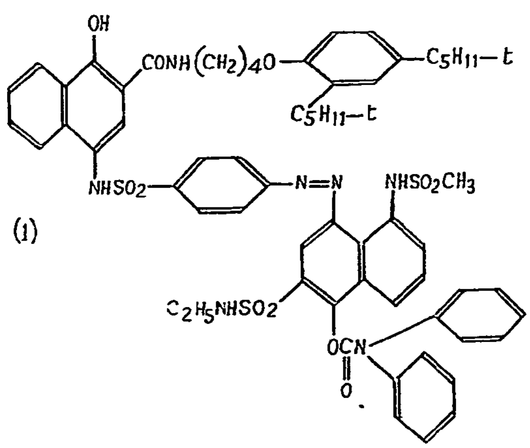
The resulting coating was permitted to dry and then was heated by contacting it with a metal block at 150°C for 30 seconds. A hue shift from yellow (maximum absorption of 450 nm) to magenta (maximum absorption of 550 nm) was observed indicating that thermal deblocking of the described dye precursor had occurred.

Example 2

A light insensitive coating was prepared by coating the following mixture of components on a poly(ethyleneterephthalate) film support:

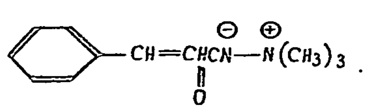
(1) shifted dye represented by the structure:

(1)



g/m^2
0.43

(2) base-release agent represented by the structure:



2.15

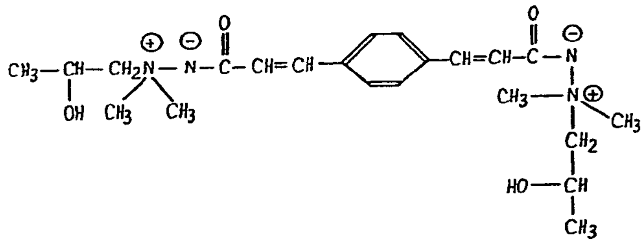
(3) gelatin (binder) 3.8

The resulting coating was permitted to dry and then was heated at 150°C as described in

Example 1. Complete conversion from the yellow, shifted dye (maximum absorption at 450 nm) to the magenta dye (maximum absorption at 550 nm) occurred. The reaction half life, measured as the time required to produce one-half the total green-light absorption (that is one-half of magenta dye) was approximately 5 seconds at 150°C.

Example 3

A coating like that described in Example 2 was prepared except that the described base-release agent was replaced with a base-release agent represented by the structure:



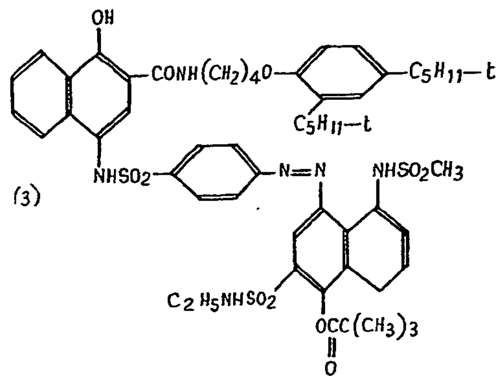
g/m²
2.15

After heating the resulting material at 150°C as described in Example 1, complete conversion from the yellow shifted dye to the magenta dye was observed with a reaction half life of approximately 15 seconds at 150°C.

Example 4

A coating like that described in Example 2 was prepared with the exception that the described dye precursor was replaced with a dye precursor (Compound 3) represented by the structure:

(3)



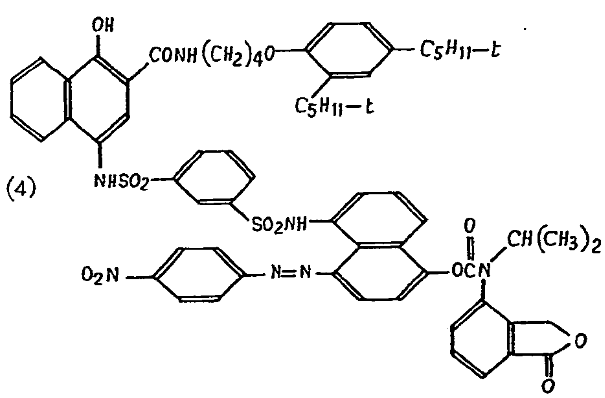
g/m²
2.15

After heating the resulting element at 150°C for 30 seconds, approximately 60% of the blocked yellow dye was converted to magenta dye.

Example 5

A coating like that described in Example 2 was prepared with the exception that the described dye precursor was replaced with a dye precursor (Compound 4) represented by the structure:

(4)



g/m²
2.15

After heating the described material at 125°C for 20 seconds, approximately 40—50% of the blocked dye (having a maximum absorption at 490 nm) was converted to the unblocked cyan dye.

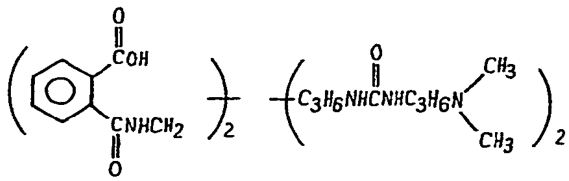
Example 6

A coating like that described in Example 4 was prepared with the exception that the described base-release agent was replaced with guanidinium trichloroacetate at 2.15 g/m^2.

After heating the resulting material at 125°C for 30 seconds, the conversion to magenta dye was nearly complete.

Example 7

A coating like that described in Example 2 was prepared with the exception that the described base-release agent was replaced with an amine salt of a phthalamic acid derivative represented by the structure:



This amine salt base-release agent was coated at 3.2 g/m^2.

The resulting material was heated at 150°C for 35 seconds as described in Example 1. Upon heating, the yellow blocked dye was converted to the described magenta dye.

Example 8

Photothermographic Silver Dye-bleach Material

A photothermographic material was prepared by coating the following components on a transparent poly(ethyleneterephthalate) film support:

Gelatino silver bromoiodide emulsion (2.5 mole% iodide)	0.65 g of silver m^2
Gelatin (binder)	8.6 g/m^2
1-phenyl-3-pyrazolidone (developing agent)	0.99 g/m^2
Base-release agent (as described in Example 7)	6.5 g/m^2
Shifted dye (Compound 1—see Example 2)	0.43 g/m^2

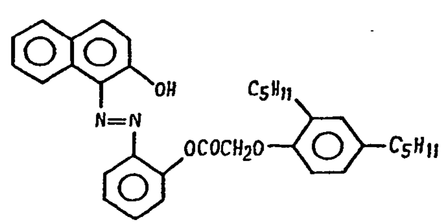
A sample of the resulting photothermographic material was imagewise exposed through a graduated density test object to light to produce a developable latent image. The material was then uniformly heated for 30 seconds by contacting it with a heated metal block at 150°C. This produced a negative silver image and a uniform distribution of magenta dye.

The photothermographic material was then laminated to a silver dye-bleach activator sheet comprising a resin coated paper support having coated thereon a layer containing the following components:

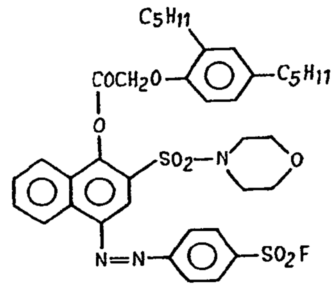
	g/m^2
Gelatin (binder)	4.6
Thiourea (complexing agent)	5.4
1,6-hexanediol (thermal solvent)	2.7
Imidazole	2.15

Prior to coating the liquid coating composition containing the thiourea, the composition was adjusted to pH 6.5 with hydrochloric acid. The resulting laminated structure was heated for 15 minutes at 110°C. After heating, the activator sheet and photothermographic material were not separated. A well-defined positive magenta dye image could be viewed through the transparent support of the latter. Hydrochloric acid in some instances may not be the optimum acid for providing the desired pH because of its volatility. Other image dye precursors that may be used include the following Compounds 5 to 11.

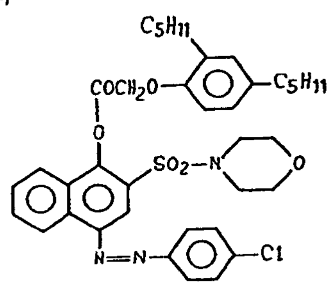
Compound 5



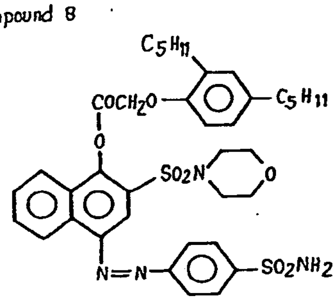
Compound 6



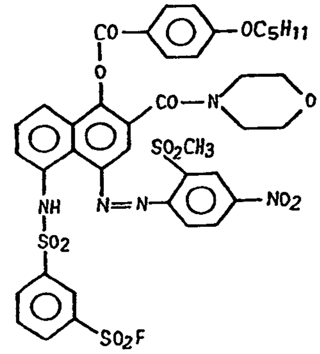
Compound 7



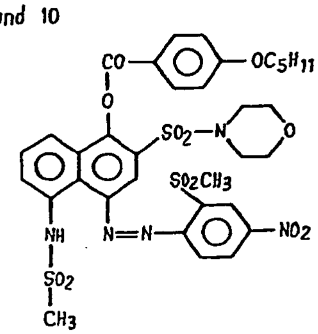
Compound 8



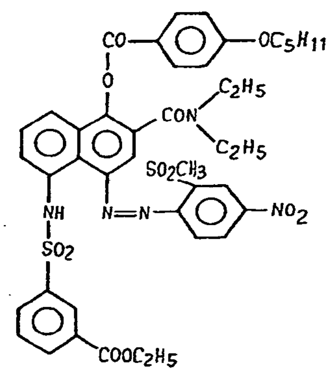
Compound 9



Compound 10



Compound 11



Claims

1. A sensitive photothermographic material which comprises a support coated on one side with at least one binder-containing layer and, incorporated in the said layer or layers, a photosensitive silver salt, a silver halide developing agent (or a precursor thereof), a base-release agent, and a precursor of an azophenol or azonaphthol image dye capable of being imagewise bleached in a silver dye-bleach process, the precursor containing a blocked auxochromic hydroxyl group which is deblocked by base released by the base-release agent when the material is heated overall to the intended processing temperature.

2. A material according to Claim 1 wherein the precursor of the azophenol or azonaphthol image dye is a compound of the general Formula I herein.

3. A material according to Claim 1 wherein the precursor of the azophenol or azonaphthol image dye is a compound of the general Formula II herein.

4. A material according to Claim 1 wherein the precursor of the azophenol or azonaphthol image dye is one of the Compounds 1 to 11 specified herein.

5. A material according to any of the preceding claims wherein the photosensitive silver salt is present as a gelatino-silver halide photographic emulsion.

6. A material according to any of the preceding claims wherein the base-release agent is an aminimide.

7. A material according to any of the preceding claims which comprises coated on the said one side of the support a silver dye-bleach activator layer containing a silver complexing agent, a diffusible acid and a thermal solvent.

8. A material according to Claim 7 wherein the activator layer contains a silver dye-bleach catalyst.

9. A material according to Claim 1 substantially as described in Example 8 herein.

10. A coating composition for use in making a sensitive photothermographic material as claimed in any of the preceding claims in which the specified constituents are incorporated in a single layer, the composition comprising a dispersion in a liquid of the specified constituents.

11. A sensitive photothermographic material which comprises a support coated with a layer of a coating composition according to Claim 10.

12. A method of forming a silver image and an azophenol or azonaphthol image dye capable of being imagewise bleached in a silver dye-bleach process which comprises imagewise exposing to light a sensitive photothermographic material according to any of Claims 1 to 6 and heating the material overall to bring about development of the desired silver image and deblock the auxochromic hydroxyl group of the azophenol or azonaphthol image dye precursor.

13. A method of forming a dye-image which comprises forming a silver image and an azophenol or azonaphthol image dye by a method according to Claim 12 and heating the silver image and dye in the presence of a silver complexing agent, an acid and, if necessary, a silver dye-bleach catalyst to bleach in proportional amounts the image silver and the image dye.

14. A method according to Claim 13 wherein the photothermographic material is heated in contact with an activator sheet containing the silver complexing agent, acid and, if present, catalyst.

15. A method according to Claim 13 wherein the photothermographic material is according to Claim 7 or 8.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.